

PATENT SPECIFICATION

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(54) SULFOSUCCINATE DERIVATIVES FOR USE AS DETERGENT BUILDERS

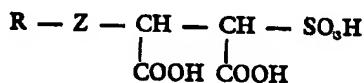
(71) We, UNILEVER LIMITED, a company organised under the laws of Great Britain, of Unilever House, Blackfriars, London, E.C.4, England, do hereby declare the 5 invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 Eutrophication is the process of excessive fertilization of aquatic plants through enrichment of waters with nutrients, such as carbon, nitrogen, phosphorus, potassium, iron, trace metals and vitamins.

15 Although there is no present adequate proof, it has been postulated that the phosphorus-containing builders present in detergent compositions can be a factor in eutrophication. Therefore any substitutes which do not contain phosphorus may decrease to some extent 20 the eutrophication.

It is therefore an object of the present invention to provide novel compounds which are useful as detergent builders. It is another 25 object of the present invention to provide novel compounds which function as surface active agents and as detergent builders.

30 It has now been discovered that the alkali metal, ammonium and substituted ammonium salts of certain sulfoaliphatic dicarboxylic acids can serve as effective detergent builders in detergent compositions. Many of these 35 detergent builders and their acid forms are novel and they are generally described as α - substituted - β - sulfosuccinic acids, and alkali metal, ammonium and substituted ammonium salts thereof, having the general formula:

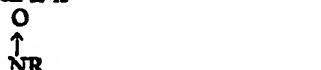


(I)

wherein Z is O, S, SO, SO₂,



or NR₁; R is (C₁—C₃₀) alkyl, (C₁—C₃₀) hydroxyalkyl or (C₂—C₃₀) alkoxyalkyl; phenyl; carboxy-substituted or mono-, di- or tri-alkyl-substituted phenyl, wherein each of the alkyl group or groups contains 1—4 carbon atoms; sulfoalkyl or carboxyalkyl, wherein the alkyl moieties contain 1—4 carbon atoms; or R'Z(CH₂CH₂O)_n—CH₂CH₂—, wherein R' is hydrogen or alkyl containing 1—24 carbon atoms; and n is 0 or an integer of from 1—15; and when Z is



55 or NR₁, the groups R may be joined with the nitrogen atom to form a morpholinyl group, and when Z is O and the group R is an alkyl group the latter contains 2—30 carbon atoms.

Thus, specific compounds and classes of compounds embraced by the generic formula above include:

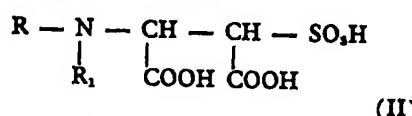
α - alkoxy - β - sulfosuccinic acids
 α - phenoxy - β - sulfosuccinic acids
 α - carboxyphenoxy - β - sulfosuccinic acids
 α - alkylphenoxy - β - sulfosuccinic acids
 α - carboxyalkoxy - β - sulfosuccinic acids
 α - sulfoalkoxy - β - sulfosuccinic acids
 α - alkoxyethoxy - β - sulfosuccinic acids
 α - alkoxypolyethyleneoxyethoxy - β - sulfosuccinic acids
 α - hydroxyalkoxy - β - sulfosuccinic acids; 60

65 the alkali metal, ammonium and substituted ammonium salts thereof; and the thio, sul-

[Price 33p]

5 finyl and sulfonyl analogs of all the foregoing compounds wherein the oxygen group attached to the α -carbon of the succinic acid or succinate moiety is replaced by $-\text{S}-$, $-\text{SO}-$ or $-\text{SO}_2-$, respectively, and/or wherein the cases of the α -alkoxyethoxy compounds and the α -alkoxypolyethyleneoxyethoxy compounds the oxygen attached to the alkyl group (R') is replaced by $-\text{S}-$, $-\text{SO}-$ or $-\text{SO}_2-$.

10 In accordance with a specific aspect of the present invention are the nitrogen containing α -substituted- β -sulfosuccinic acids, and the alkali metal, ammonium and substituted ammonium salts thereof, having the following general formula:



20 wherein the groups R and R_1 may be the same or different and R_1 is C_1 to C_{20} alkyl, C_1 to C_4 hydroxyalkyl, carboxymethyl, carboxyethyl, sulfomethyl or sulfoethyl, or R and R_1 may be joined with the Nitrogen atom to form a morpholinyl moiety; and R_1 is hydrogen or R .

25 Representative compounds and classes of compounds embraced by generic Formula II above include:

30 α -alkylamino- β -sulfosuccinic acids such as α -methylamino, α -propylamino, α -octylamino and α -laurylamino- β -sulfosuccinic acid;

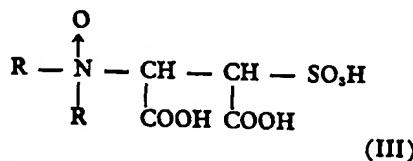
35 α -dialkylamino- β -sulfosuccinic acids such as α -dimethylamino, α -ethylmethylamino, α -methylhexylamino and α -di-octylamino- β -sulfosuccinic acid;

40 α -hydroxyalkylamino- β -sulfosuccinic acids such as α -hydroxyethylamino, α -hydroxybutylamino and α -bis(hydroxyethyl)amino- β -sulfosuccinic acid;

45 α -carboxyalkylamino- β -sulfosuccinic acids such as α -carboxymethylamino, α -carboxyethylamino- β -sulfosuccinic acid and the corresponding sulfo analogs;

50 α -morpholinyl- β -sulfosuccinic acid; and the mono or poly salts thereof.

In accordance with further specific aspect of the present invention are the amine oxide derivatives of Formula II, wherein the nitrogen is a tertiary atom, corresponding to the general formula:



wherein the groups R may be the same or different and are as designated in Formula II.

As will be appreciated by those skilled in the art, the compounds of the invention contain at least two asymmetric carbon atoms and therefore can exist in several optically active forms as well as optically inactive mixtures (racemates). For purposes of this invention, the compounds as defined are intended to include all of the stereoisomeric forms and mixtures thereof.

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In addition to the detergent building properties exhibited by the entire class of compounds described above, certain select members also exhibit properties which make them useful as wetting and foaming agents and thus constitute a class of novel surface active agents. For example, the α -alkoxy- β -sulfosuccinic acids and the thio analogs, containing from about 1-8 carbons, preferably from 1 to about 4 carbon atoms, exhibit excellent detergent building properties whereas the higher homologs containing from about 9-30 and more preferably 9-24 carbon atoms in the alkyl chain, additionally exhibit wetting, foaming and detergency properties.

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Similarly, the α -alkoxyethyl and α -alkoxypolyethyleneoxyethoxy- β -sulfosuccinic acid compounds containing from about 9-30 and preferably about 9-24 carbon atoms in the alkoxy moiety are also useful as wetting agents, foaming agents and detergents as well as detergent builders.

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Although the builders of the present invention may be utilized as the free acid provided sufficient alkaline additives are included in the detergent composition to convert the acid forms in situ to the normal salt forms, the alkali metal, ammonium and substituted ammonium salts of the α -substituted- β -sulfosuccinic acids are preferred. Included in the substituted ammonium salts that can be employed are the monoethanolammonium, diethanolammonium, triethanolammonium, methylammonium, dimethylammonium, trimethylammonium, tetramethylammonium, morpholinium, N-methylmonoethanolammonium and N-ethylmonoethanolammonium salts and mixtures thereof.

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The utility of the compounds of the present invention is not only reflected in terms of excellent building and biodegradability properties but also in low cost of preparation, since they are prepared from readily available and inexpensive materials. For example, the compounds of this invention are derived from sulfomaleic anhydride and readily available alcohols, thiols, hydroxy acids and amines.

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More specifically, the compounds of this invention are reaction products derived by reaction between sulfomaleic acid and compounds having an active hydrogen atom.

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Compounds having an active hydrogen atom and suitable for use in preparing the compounds of the present invention are mono- di- or polyhydric alcohols and mono- di- or polyhydroxy acids and their sulfur-containing

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		analog. Suitable examples of the aforementioned monohydric alcohols include alkoxy-alkanols such as methoxyethanol and the linear primary and secondary alcohols containing up to 30 carbon atoms and their thio analogs; aromatic hydroxy compounds particularly the carbocyclic mono- and bicyclic aromatic hydroxy compounds, such as naphthols and phenols and the mono- di- or tri- C_1-C_4 alkyl ring substituted derivatives thereof. Suitable examples of dihydric alcohols include the glycols such as ethylene glycol, propylene glycol, butylene glycol, trimethylene glycol, tetramethylene glycol, pentamethylene glycol, hexamethylene glycol, heptamethylene glycol, long chain 1,2-diols containing from 8-30 carbon atoms and aromatic carbocyclic glycols such as phenylethylene glycol. Similarly, suitable polyhydric alcohols include glycerol, pentaerythritol, hexanetriol, sugars and their thio analogs.	form the α - substituted amino - β - sulfosuccinates include:	65
5			ethanolamine	
			diethanolamine	
			propanolamine	
			morpholine	70
			N-methylethanolamine	
			glycine	
			alanine	
			N-methyl taurine	
10			alkylamines containing 1-20 carbons in the alkyl chain, as well as other amines having a replaceable or active hydrogen and a basicity comparable to the aforementioned amines.	75
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25			In particular the α -amino substituted- β -sulfosuccinates derived from water-soluble amines may be prepared by reacting in aqueous solution without the aid of heat and those derived from water-insoluble amines (i.e., higher alkylamines) are reacted in a mixed solvent system such as ethanol/water or dioxane/water at temperatures ranging from about 25° C to about 80° C; isolation from the reaction medium, and purification if desired, being effected by conventional methods.	80
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35			The compounds wherein the α -substituent is joined to the α -carbon atom by an amine oxide group (as in Formula III) may be prepared by reacting the tertiary amine compounds of Formula II with oxidizing agents such as hydrogen peroxide, peroxyacetic and peroxyformic acid in the manner described for oxidizing tertiary amines by Hoh et al., J. Am. Oil Chemists' Soc., 40, 268 (1963).	85
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50			In preparing the sulfosuccinate salts from the free acid, the amount of base utilized will determine whether the mono- di- or tri-salt is obtained. For example, the use of one mole of base (i.e., sodium hydroxide) per mole of α -hydroxy- β -sulfosuccinic acid yields the monosodium salt; the use of two moles of sodium hydroxide, the disodium salt and the use of three moles of sodium hydroxide, the trisodium salt. When R is carboxymethyl, carboxyethyl, sulfomethyl or sulfoethyl, a tetrasalt can also be obtained. Similarly, other bases, such as ammonium hydroxide and organic amines, may be utilized in the same manner to afford the type of salt desired.	90
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60			According to the present invention, excellent cleaning results can be obtained by using the novel compounds described above as detergency builders with a wide range of detergent surface active materials and mixtures thereof in any of the usual physical forms for such compositions such as powders, beads, flakes, bars, tablets, noodles, liquids and the like. The builders can be used singularly, in combination with each other as the sole builder in the detergent composition or in combination	105
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with other well-known detergent builders such as sodium nitrilotriacetate, sodium ethylenediaminetetraacetate, sodium tripolyphosphate, trisodium orthophosphate, sodium and potassium pyrophosphate, sodium polyacrylate, disodium oxydiacetate, trisodium citrate, tri-sodium carboxymethoxy succinate, salts of oxidized starches and sodium or potassium carbonate, as well as other conventional organic and inorganic builders.

When using the detergent compositions to wash clothes, the wash solutions should have a pH from about 7 to 12 and preferably from 9 to 11 throughout the washing cycle. Therefore, the presence of an alkaline buffer in the detergent composition is usually desirable particularly when the soil to be removed from the clothes has a high content of acidic components. Suitable buffers include any of the common organic and/or inorganic buffers such as monoethanolamine, diethanolamine, triethanolamine, sodium and potassium silicates, sodium and potassium carbonates and bicarbonates and the like.

In the detergent compositions, which are claimed in our copending divisional application No. 785/75 (Serial No. 1,398,422), the only essential ingredients are the detergent surface active material and the builder. The weight percent of the builder present in the detergent composition will range from 5 to 90% and preferably from 20 to 60% and more preferably 35—50% by weight of the total weight of the composition. When expressed as a weight ratio of builder to surfactant, the builders used in the instant invention will generally be present in a ratio of about 1:10 to about 10:1, and preferably 2:1 to 5:1 depending on the end use of whether a heavy-duty or light-duty detergent is desired. When the builders are used in mechanical dishwashing compositions, the ratio of builder to surfactant is from about 10:1 to about 50:1.

The detergent surface active compounds which can be used within the detergent compositions include anionic, nonionic, zwitterionic, ampholytic detergent compounds and mixtures thereof. A detailed description of such detergent compounds is to be found in the Specification of our Divisional Application referred to above.

Other materials which may be present in the detergent compositions in generally minor amounts are those conventionally present therein. Typical examples thereof include the well-known soil-suspending agents, hydro-tropes, corrosion inhibitors, dyes, perfumes, fillers such as sodium sulfate, optical brighteners, perborates, bleaches, bleach activators, enzymes, suds boosters, suds depress-

ants, germicides, fungicides, anti-tarnishing agents, cationic detergents, fabric softening agents and in the case of liquid compositions, opacifiers and organic solvents. The balance of the detergent compositions may be water or inert filler.

It has been discovered that when higher than normal levels of anionic, nonionic, ampholytic or zwitterionic surfactants are used with the sulfosuccinate derivative salts of this invention, the detergency of the formulation is significantly enhanced particularly at low formulation concentrations (~ 0.1%) which are typically used by the housewife. For enhanced results the detergent formulation should contain surfactant levels of about 25% to about 45% by weight and the sulfosuccinate derivative salt levels of about 25% to about 75% by weight in the cases where the surfactants are anionic, ampholytic or zwitterionic. When the surfactant is a nonionic, enhanced detergency results are obtained when the level of said nonionic in the formulation is from about 15% to 30% by weight and the level of sulfosuccinate derivative salt is from about 25% to about 85% by weight.

In addition to their use in general household detergent compositions, the builders of the present invention find utility as boiler scale removers, stain removers and general chelating agents. When used at pH's of about 2 to about 5 as partially neutralized alkali metal, ammonium or substituted ammonium salts, especially in combination with wetting agents and surfactants, the compounds of the invention are excellent metal cleaning compounds.

EXAMPLE 1.

Table 1 below illustrates detergent compositions containing the detergency builders of the present invention in combination with representative classes of surface active agents compared with control or standard phosphate-built detergent compositions. The compositions were prepared by blending together the recited components in the proportions indicated, including an anticorrosive agent and buffer agent (sodium silicate), and the balance being water. The compositions were then tested on vacuum cleaner dust soiled cloth for detergency or cleaning ability in the Terg-O-Tometer test; wherein washing conditions are as indicated and the results reported as detergency units. The average detergency units (DU) of the formulation is the final reflectance of the soiled cloth, the reflectances being obtained by measurement with a Gardner automatic color difference meter, Model AC-3.

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TABLE I

Component	% Composition					Controls (% Composition)				
α -hydroxy ^a	50	50	50	50	50					
α -(2-hydroxy- ϵ -ethoxy) ^a			50	50						
α -dodecyloxy ^a				50						
α -methoxy ^a					50					
α -carboxymethoxy ^a										
α -dodecyloxyethoxy ^a						50				
α -dodecylothio ^a							50			
$Na_3P_3O_{10}$	10	10	10	10	10					
Sodium silicate ($SiO_2:Na_2O=2:4:1$)						10	10	10	10	10
Anionic ^b	18		18	18	18					
Anionic ^c		18					18		18	
Nonionic ^d		20					20		20	
Amphotytic ^e			18							
Zwitterionic ^f			18					18		
Water										balance
Formulation Concentration, %	0.2	0.2	0.2	0.2	0.1	0.2	0.2	0.2	0.2	0.2
Detergency (DU's)	24.6	24.4	26.5	23.1	25.6	26.1	24.7	27.1	23.0	24.2
									15.4	22.3
									4.8	6.4
									16.1	19.9
									18.8	20.1
									28.7	29.4
									28.5	28.5

5 ^aSodium salts of α -substituted- β -sulfosuccinate
^bSodium linear secondary alkyl (C_{10} - C_{15}) benzene sulfonate
^cSodium C_{15} - C_{18} α -olefin sulfonate
^d C_{11} - C_{15} linear secondary alcohols ethoxylated with 7 moles ethylene oxide/mole alcohol
^e C_{14} - C_{18} HAMT (sodium hydroxylalkyl N-methyl taurate)
^fSulfobetaine DCH (cocodimethylsulfopropyl betaine)
10 Washing conditions—180 ppm (2:1 Ca^{++} / Mg^{++}); 120° F; pH 10
15 The following Examples 2 to 11 show the preparation of α -substituted- β -sulfo-succinates.

EXAMPLE 2.
Preparation of Trisodium α -thio substituted- β -Sulfosuccinate

20 Sulfomaleic anhydride was prepared by heating a mixture of 1 mole of sulfur trioxide with 1 mole of maleic anhydride first at 60° C until the exothermic reaction subsided and then at 100—110° C for 3 hours. Forty-five gm of sulfomaleic anhydride product was then mixed with 45 gm of ice and the resulting solution extracted 25 times with 50 ml portions of ether to remove maleic acid. A 20 ml portion of the resulting aqueous phase was collected, adjusted to pH = 8.6 with sodium hydroxide and refluxed for 4 hours. Then, an aqueous solution containing excess sodium methyl or ethyl mercaptide is added and the resulting solution allowed to stand overnight. The reaction mixture is then passed through a column of cation exchange resin and the effluent to low volume. The pH is then adjusted to 8.5 with sodium hydroxide and the solution evaporated to dryness. In this way, there is afforded trisodium α -methylthio- β -sulfosuccinate or trisodium α -ethylthio- β -sulfosuccinate.

EXAMPLE 3.
Preparation of Trisodium α -Ethoxy- β -Sulfosuccinate

45 Sulfomaleic anhydride, 3.9 gm, was dissolved in 25 ml of ethanol and refluxed for 5 hours. Then, 24 gm of 25% sodium ethoxide in ethanol was added and the solution was refluxed for 2 hours. The ethanol was then evaporated and the residue was dissolved in 100 ml of water and heated for 1 hour at 80° C. The solution was then decolorized with 5 gm of charcoal, filtered and evaporated. The crude residue of trisodium α -ethoxy- β -sulfosuccinate was purified by trituration with acetic acid and then filtered, washed with acetone and dried.

EXAMPLE 4.
Preparation of Trisodium α -Dodecyloxy- β -Sulfosuccinate

60 Sulfomaleic anhydride (10 gm) are mixed with 80 gm (0.45 mole) of n-dodecanol and heated at 100° C for 14 hours. A solution of 7.04 gm of sodium hydroxide in 50 ml water is then added and the mixture heated at 60° C for 2 hours. The heated mixture is then extracted three times with 300 cc portions of acetone (at reflux) and the acetone insoluble fraction is then filtered, washed with additional acetone and dried to give 16.2 gm of the title compound (structure confirmed by NMR and ion exchange of a sample followed by titration with standard sodium hydroxide: neutralization equivalent: found 147.0, theory 149.3).

EXAMPLE 5.
Preparation of Trisodium α -Dodecyloxy-ethoxy- β -Sulfosuccinate

Using the procedure of Example 4 and substituting 37 gm (0.32 mole) of 2-dodecyloxyethanol in place of the n-dodecanol there is obtained trisodium α -dodecyloxyethoxy- β -sulfosuccinate.

EXAMPLES 6—8.

Using n-tetradecanol in place of n-dodecanol in the procedure of Example 4 and carrying out the hydrolysis step with 10% excess aqueous sodium hydroxide at 80° C for 4 hours instead of 60° C at 2 hours, there is obtained trisodium α -tetradecyloxy- β -sulfosuccinate (Example 6). Similarly, using n-hexadecanol in place of n-dodecanol, there is obtained trisodium α -hexadecyloxy- β -sulfosuccinate (Example 7); using n-octadecanol, there is obtained trisodium α -octadecyloxy- β -sulfosuccinate (Example 8).

EXAMPLE 9.
Preparation of Trisodium α -Hydroxyethoxy- β -Sulfosuccinate

Sulfomaleic anhydride (20 gm) is mixed with 37.2 gm (0.6 mole) of ethylene glycol and heated at 80° C for 4 hours. A solution of 16 gm (0.4 mole) of sodium hydroxide in 75 ml of water is then added and the mixture heated at 80° C for 4 hours. The mixture is then mixed with acetone to precipitate trisodium α -hydroxyethoxy- β -sulfosuccinate, which is purified by repeated extractions with hot acetone to remove all ethylene glycol and water followed by filtration and drying in an oven.

EXAMPLE 10.
Preparation of the Tetrasodium Salt of α -Carboxymethoxy- β -Sulfosuccinic Acid

Sulfomaleic anhydride (19.4 gm) is heated to 60° C and combined with 76 gm of ethyl glycolate. After heating the mixture at 80° C for 5 1/2 hours, there is added a solution of 45 gm of sodium hydroxide dissolved in 135 gm of water and heating is continued at 80° for an additional three hours. The mixture is then diluted with water and passed through a column of a cation exchange resin. The resulting eluent is then evaporated in vacuo to

5 a low volume and the concentrate extracted repeatedly with acetone to remove glycolic acid and other impurities. The resulting extracted residue is then dissolved in water and the pH of the solution adjusted to 8.6 with dilute sodium hydroxide. Evaporation of the solution in vacuo and drying over P_2O_5 gives a residue of the tetrasodium salt of α -carboxymethoxy- β -sulfosuccinic acid.

10 EXAMPLE 11.

Preparation of Trisodium α -(2-Hydroxy-ethylamino)- β -Sulfosuccinate

15 Sulfomaleic anhydride (prepared from a 1/1 ratio of SO_3 /maleic anhydride by heating the mixture at 100-110° C for 3 hours; active content, 86%) 20.7 gm (0.1 mole), was added to 100 gm of ice. The resulting solution was kept at 10-15° C and neutralized to pH = 8.6 by slowly adding 28.4 gm of 50% sodium hydroxide. Monoethanolamine, 6.1 gm (0.1 mole), was next added slowly and the temperature allowed to rise to room temper-

ature. After standing overnight, the reaction mixture was poured into 800 ml of acetone. The solvent was then decanted from the resulting syrupy lower layer and the latter reprecipitated three times from water with fresh acetone. The residue was then dried in a desiccator over P_2O_5 , to give 38.8 gm of an off-white, granular product containing approximately 88% trisodium - α - (2 - hydroxyethylamino) - β - sulfosuccinate by titration with perchloric acid. The structure was confirmed by NMR analysis.

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The above method is satisfactory for reacting water-soluble amino compounds with sulfomaleic anhydride. For water insoluble amino compounds such as the higher alkyl amines, a mixed solvent system such as ethanol/water and dioxane/water is used together with temperatures in the range of 25-80° C.

Table 2 indicates the reactants required to obtain other α - substituted - β - sulfosuccinate salts having the R and Z moieties set forth in Formula I, following the procedures of the appropriate examples.

TABLE 2
Example Reactants (Sulfomaleic Anhydride +)

R	Z	Example
Ethyl	0	3 ethanol
Alkyl (C ₁ –C ₃)	0	4–8 C ₁ –C ₃ primary, secondary or tertiary alcohol
Phenyl	0	4–8 Phenol
Carboxyphenyl	0	10 Methyl salicylate
(C ₁ –C ₃) Alkylphenyl	0	4–8 (C ₁ –C ₃) Alkylphenol
o, m, p methylphenyl or methylisopropyl phenyls	0	4–8 o, m, p cresol, carvacrol, thymol
HOOC–CH ₂ –	0	10 Ethyl glycolate
HOOC–CH ₂ CH ₂ –	0	10 Methyl- β -hydroxypropionate
HO ₂ S–CH ₂ CH ₂ –	0	4 Isethionic acid
R' O(CH ₂ CH ₂ O) _n –CH ₂ CH ₂ –	0	4 R' O(CH ₂ CH ₂ O) _n CH ₂ CH ₂ OH
HOCH ₂ CH ₂ OCH ₂ CH ₂ –	0	4 HOCH ₂ CH ₂ OCH ₂ CH ₂ OH
HO(CH ₂ CH ₂ O) ₂ CH ₂ CH ₂ –	0	4 HO(CH ₂ CH ₂ O) ₂ CH ₂ CH ₂ OH
HO(CH ₂ CH ₂ O) ₃ CH ₂ CH ₂ –	0	4 HO(CH ₂ CH ₂ O) ₃ CH ₂ CH ₂ OH
HO(CH ₂ CH ₂ O) ₄ CH ₂ CH ₂ –	0	4 HO(CH ₂ CH ₂ O) ₄ CH ₂ CH ₂ OH
CH ₃ CH ₂ O(CH ₂ CH ₂ O) ₂ CH ₂ CH ₂ –	0	4 CH ₃ CH ₂ O(CH ₂ CH ₂ O) ₂ CH ₂ CH ₂ OH
CH ₃ (CH ₂) ₂ O(CH ₂ CH ₂ O) ₃ CH ₂ CH ₂ –	0	4 CH ₃ (CH ₂) ₂ O(CH ₂ CH ₂ O) ₃ CH ₂ CH ₂ OH
CH ₃ (CH ₂) ₃ O(CH ₂ CH ₂ O) ₄ CH ₂ CH ₂ –	0	4 CH ₃ (CH ₂) ₃ O(CH ₂ CH ₂ O) ₄ CH ₂ CH ₂ OH
CH ₃ CH ₂ S(CH ₂ CH ₂ O) ₂ CH ₂ CH ₂ –	0	4 CH ₃ CH ₂ S(CH ₂ CH ₂ O) ₂ CH ₂ CH ₂ OH
CH ₃ CH ₂ S(CH ₂ CH ₂ O) ₃ CH ₂ CH ₂ –	0	4 CH ₃ CH ₂ S(CH ₂ CH ₂ O) ₃ CH ₂ CH ₂ OH

TABLE 2 (Continued)

R	Z	Example Reactants (Sulfomaleic Anhydride +)
$\text{HOCH}_2\text{CH}_2-$	0	9 Ethylene glycol
$\text{HOCH}_2\text{CH}_2\text{CH}_2-$	0	9 Trimethylene glycol
$\text{HOCH}_2(\text{CH}_2)_4\text{CH}_2-$	0	9 Hexamethylene glycol
Methyl or ethyl	S	2 Sodium methyl or ethyl mercaptide
Alkyl (C_3-C_{10})	S	4-8 C_3-C_{10} alkylmercaptan
Phenyl	S	4-8 Thiophenol
Carboxyphenyl	S	10 Methyl 2-mercaptopbenzoate
Alkylphenyl	S	4-8 Alkylthiophenol
$\text{HOOC-CH}_2-\text{CH}_2-$	S	10 Ethyl mercaptoacetate
$\text{HOOC-CH}_2-\text{CH}_2-\text{CH}_2-$	S	10 Methyl β -mercaptopropionate
$\text{HO}_2\text{SCH}_2\text{CH}_2-$	S	4 Mercaptoethanesulfonic acid
$\text{R}'\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2-$ *	S	4 $\text{R}'\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{SH}^*$
$\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$	S	2 $\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{SNa}$
$\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2-$	S	2 $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{SNa}$
$\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2-\text{CH}_2\text{CH}_2-$	S	2 $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{SNa}$
$\text{CH}_3\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2-$	S	4 $\text{CH}_3\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{SH}$
$\text{CH}_3(\text{CH}_2)_n\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2-$	S	4 $\text{CH}_3(\text{CH}_2)_n(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{SNa}$
$\text{CH}_3(\text{CH}_2)_n\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2-$	S	4 $\text{CH}_3(\text{CH}_2)_n(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{SH}$

TABLE 2 (Continued)

R	Z	Example	Reactants (Sulfomaleic Anhydride +)
$\text{CH}_3\text{CH}_2\text{S}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{I}$	S	4	$\text{CH}_3\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{SH}$
$\text{CH}_3\text{CH}_2\text{S}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{I}$	S	4	$\text{CH}_3\text{CH}_2\text{S}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{SH}$
$\text{HOCH}_2\text{CH}_2\text{I}$	S	2	Sodium 2-hydroxyethylmercaptoide
$\text{HOCH}_2\text{CH}_2\text{CH}_2\text{I}$	S	2	Sodium 3-hydroxypropylmercaptoide
$\text{HOCH}_2(\text{CH}_2)_4\text{CH}_2\text{I}$	S	2	Sodium 6-hydroxyhexylmercaptoide
Methyl or ethyl	SO	2	Methyl or ethyl mercaptana
Alkyl ($\text{C}_1\text{--C}_{10}$)	SO	4-8	$\text{C}_1\text{--C}_{10}$ alkylmercaptana
Phenyl	SO	4-8	Thiophenol a
Carboxyphenyl	SO	10	Methyl 2-mercaptopbenzoate a
$\text{C}_1\text{--C}_4$ alkylphenyl	SO	4-8	Alkylthiophenol a
$\text{HOOC--CH}_2\text{I}$	SO	10	Ethylmercaptopacetate a
$\text{HOOC--CH}_2\text{CH}_2\text{I}$	SO	10	Methyl β -mercaptopropionate a
$\text{R}'\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{I}^*$	SO	5	$\text{R}'\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{SH}^a$ *
$\text{HOCH}_2\text{CH}_2\text{I}$	SO	2	Sodium 2-hydroxyethylmercaptoide
$\text{HO}(\text{CH}_2\text{CH}_2)_4\text{CH}_2\text{I}$	SO	2	Sodium 6-hydroxyhexylmercaptoide
a Followed by oxidation to sulfoxide according to Fieser reference.			
$\text{C}_1\text{--C}_4$ alkyl	SO ₂	2	$\text{C}_1\text{--C}_2$ alkylmercaptan b
$\text{C}_1\text{--C}_{10}$ alkyl	SO ₂	4-8	$\text{C}_1\text{--C}_{10}$ alkylmercaptan b

TABLE 2 (Continued)

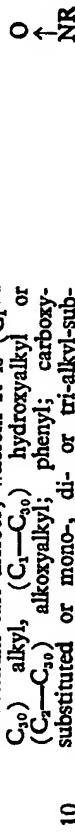
R	Z	Example Reactants (Sulfomaleic Anhydride +)
Phenyl	SO ₂	4-8 Thiophenol ^b
Carboxyphenyl	SO ₂	4-8 Methyl 2-mercaptopbenzoate ^b
HOOC-CH ₂ -	SO ₂	10 Ethyl mercaptoacetate ^b
HOOC-CH ₂ CH ₂ CH ₂ -	SO ₂	10 Methyl 2-mercaptopbutyrate ^b
R' O(CH ₂ CH ₂ O) _n CH ₂ CH ₂ -*	SO ₂	5 R' O(CH ₂ CH ₂ O) _n CH ₂ CH ₂ SH ^b *
b Followed by oxidation to sulfone according to Fieser reference.		
* wherein R ₁ is hydrogen or a C ₁ -C ₁₈ alkyl group.		

WHAT WE CLAIM IS:—

1. An α -substituted - β - sulfosuccinic acid having the general formula:



or NR, wherein R₁ is hydrogen or R as defined above; when Z is



or an alkali metal, ammonium or substituted ammonium salt thereof; wherein R is (C₁-C₁₀) alkyl, (C₁-C₁₀) hydroxyalkyl or (C₂-C₁₀) alkoxyalkyl; phenyl; carboxyl substituted or mono-, di- or tri-alkyl-substituted phenyl wherein each of the alkyl or carboxylalkyl wherein the alkyl moieties contain 1-4 carbon atoms; sulfoalkyl group contains 1-4 carbon atoms; or



and when Z is O and the group R is an alkyl group, the latter contains 2-30 carbon atoms.

wherein R' is hydrogen or alkyl containing 1-24 carbon atoms and n is 0 or an integer of 1-15; and Z is O, S, SO₂, SO,

20 or NR, wherein R₁ is hydrogen or R as defined above; when Z is



or NR, the groups R may be joined with the nitrogen atom to form a morpholinyl group, and when Z is O and the group R is an alkyl group, the latter contains 2-30 carbon atoms.

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2. A compound as claimed in claim 1 wherein Z is oxygen. 40

3. A compound as claimed in claim 1 or claim 2 wherein R is an alkyl group containing 2-24 carbon atoms. 45

4. A compound as claimed in claim 3 wherein R is an alkyl group containing 9-24 carbon atoms. 50

5. A compound as claimed in claim 3 wherein R is an alkyl group containing 2-8 carbon atoms. 55

6. α - dodecyloxy - β - sulfosuccinic acid or an alkali metal, ammonium or substituted ammonium salt thereof. 60

7. α - hexadecyloxy - β - sulfosuccinic acid or an alkali metal, ammonium or substituted ammonium salt thereof. 65

8. α - octadecyloxy - β - sulfosuccinic acid or an alkali metal, ammonium or substituted ammonium salt thereof. 70

9. An α -hydroxyalkoxy (2-24 carbon atoms)- β -sulfosuccinic acid or an alkali metal, ammonium or substituted ammonium salt thereof. 75

10. A hydroxyethoxy compound as claimed in claim 9. 80

11. An α -alkoxy (1-24 carbon atoms)-ethoxy- β -sulfosuccinate as claimed in claim 1. 85

12. α - dodecyloxyethoxy - β - sulfosuccinic acid or an alkali metal, ammonium or substituted ammonium salt thereof. 90

13. A compound as claimed in claim 1 wherein R is a carboxymethyl group. 95

14. A compound as claimed in claim 1 wherein Z is sulfur. 100

15. A compound as claimed in claim 14 wherein R is an alkyl group containing 1-24 carbon atoms. 105

16. A compound as claimed in claim 14

wherein R is an alkyl group containing 1-8 carbon atoms. 40

17. α - dodecylthio - β - sulfosuccinic acid or an alkali metal, ammonium or substituted ammonium salt thereof. 45

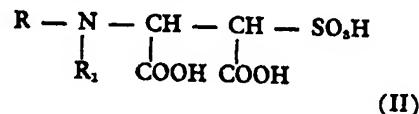
18. α - hexadecylthio - β - sulfosuccinic acid or an alkali metal, ammonium or substituted ammonium salt thereof. 50

19. α - octadecylthio - β - sulfosuccinic acid or an alkali metal, ammonium or substituted ammonium salt thereof. 55

20. A compound as claimed in claim 1 wherein Z is SO. 60

21. A compound as claimed in claim 1 wherein Z is SO₂. 65

22. A compound as claimed in claim 1 having the general formula:



wherein the groups R and R₁ may be the same or different, and R is C₁-C₂₀ alkyl; C₁-C₄ hydroxyalkyl; carboxymethyl; carboxyethyl; sulfomethyl; sulfoethyl; or R and R₁ may be joined with the nitrogen atom to form a morpholinyl moiety; and R₁ is hydrogen or R.

23. A compound as claimed in claim 1 substantially as described herein with reference to any of Examples 2-11 and in Table 2.

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